Letters to the Editor

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H.M.O. CALCULATIONS ON TETRABENZONAPHTHALENE

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(*Received September* 19, 1966 ;
Resubmitted Aprii 26, 1967)

Tetrabenzonaphthalene (fig. I) has been reported (Lang, et. al, 1961) to be a product of pyrolysis of fluorene. Recently it (Lewis, *et al*, 1963) has been identified as one of the rearrangement products of 9—9′ bifluorenylidine at 460°C. This compound is thermally stable, alternant hydrocarbon. The ultravilet spectra of this compound was observed (Lewis *et al*, 1963) at 350mμ for the longest wave length $\pi \rightarrow \pi$ transition.

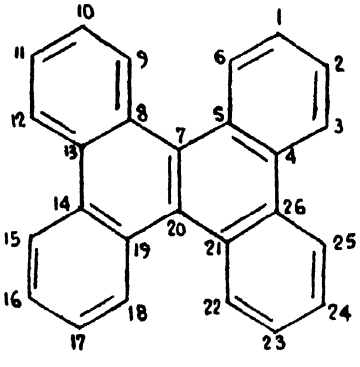

Fig. 1

The object of the present investigation is to make M.O. calculations on this molecule to see what information can be obtained about this molecule theoretically.

The method of calculation is well-known (Basu, 1954). Tetrabenzonaphthalene I belongs to the point group D_2h. Eliminating the plane of molecules which

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transforms all the p_2 atomic orbitals in the same way, it is sufficient to consider the symmetry group C_2 for molecule. The various M.O. species corresponding to different representations has been point out.

The secular equations obtained after expanding the secular determinants corresponding to different M.O. species were solved for the energy values by IBM 1620. The charge densities q bond order p and free valence index F were calculated from the coefficients and is given in table I.

The $\pi \rightarrow \pi$ logest wave length transition is calculated from the difference of energy between highest occupied level to lowest unoccupied level. The above transition is from A_1 to B_2 involving energy of the amount 1.0229β.

TABLE I

Charge densities, bond order and free valence index at different positions.

Charge densities q_t	Bond order P_{rs}	Free valence index F_r
$q_1 = .99993$	$p_{12} = .62909$	$F_1 = .40290$
$q_2 = .99924$	$p_{13} = .69401$	$F_2 = .40895$
$q_3 = 1.00001$	$p_{34} = .59666$	$F_3 = .44138$
$q_4 = 1.00003$	$p_{45} = .550787$	$F_4 = .14087$
$q_5 = 1.00000$	$p_{56} = .58972$	$F_5 = .13281$
$q_6 = 1.00002$	$p_{16} = .70006$	$F_6 = .44227$
$q_7 = 1.00008$	$p_{57} = .458745$	$F_7 = .18383$
	$p_{44} = .44375$	
	$p_{77} = .63074$	

Using the equation (Streitweiser, 1961)

$$\nu(c_m^{-1}) = (19020-330)\Delta m+(10520-340) \quad \ldots (7)$$

where $\Delta m = 1.0229$, the calculated value of λ_{max} for p band is found to be 341mμ. The observed value is 350mμ.

Symmetrical fusion of 4 benzene rings to the naphthalene nucleus offers some interesting modifications in the bond length of the parent hydrocarbon. In the resulting hydrocarbon the original 9-10 bond of the naphthalene has shortened further owing to the fusion of benzene rings as it is evident from the following M.O. diagram (fig. 2) of naphthalene (Coulson *et al*, 1965).

$p_{12} = .72456$ $\quad p_{9-10} = .51823$ $\quad F_1 = .45279$

$p_{23} = .60317$ $\quad F_2 = .40432$

$p_{19} = .5547$ $\quad F_{10} = .10442$

In case of naphthalene, F_r is the highest in position I and for tetrabenzonaphthalene it is in position (6) and (3). It has been pointed out that self atom polarizability values π_{rr} runs almost parallel to the F_r value (although no linear

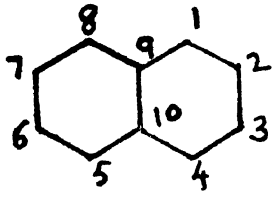

Fig. 2

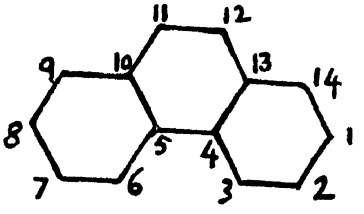

Fig. 3

relationship between them exists). The position of highest F_r is thus the most reactive position for the substitution reaction (nucleophillic or electrophilic attack). Thus position (6) is the most reactive position in tetrabenzonaphthalene.

In phenanthrene the positions of highest reactivity are positions 11 and 12

$$p_{11-12} = 0.63074$$

in this sense ($F_r = 0.45147$). The next reactive position is $14(F_r = 0.45011)$ and next to it is position $3(F_r = .44052)$. Tetrabenzonaphthalene results by the fussion of two phenantlarene rings. Naturally no substitution can take place in 11 and 12 positions. But the order of reactivity in other positions remain the same.

If HX or X_2, where X is a monovalent radical, addition takes place, the bond with highest bond order is expected to be attacked first. Here it is 1 to 6 bond in tetrabenzonaphthalene. Comparing other cases also it may be said that in one of the two bonds near the atom of highest Fr, the ease of addition will be maximum.

The total π-energy of the system Tetrabenzonapthalene is 36.7891β. Hence, 10.7891β is the delocalisation energy of the π-electrons in this net work. Thus the annealation energy (Brown, 1950) A of this system formed by fusing symmetrically 4-benzene rings into a naphthalene ring is $(11.683-10.789)\beta = .8937\beta$. Using the equation—

$$A = (2.1533\sqrt{P_a P_b} - 1.73251)\beta \qquad \ldots (9)$$

where A = annelation energy and P_a and P_b are the bond orders at the position of fusions, and taking P_a for benzene to be .667 and P_b for 1-2 bond in naphthalene to be.725 we get $A = .9436\beta$. The agreement is quite satisfactory. The equation was first proposed to consider the fusion of two systems. But, however, if Tetrabenzonaphthalene is formed by fusion of 2-phenanthrene rings, A from the equation comes to be $.0645\beta$ whereas from difference of theoretical D.E. it is $.1075\beta$.

The authors' thanks are due to Prof. S. K. Bhattacharyya for his encouragement and to Sri A. K. Maiti for help in computational work.

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